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COATED STEEL SHEET HAVING EXCELLENT CORROSION RESISTANCE
[Taishokusei Ni Sugureta Toso Koban]

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[Claims] /2[*]

[Claim 1] A coated steel sheet having excellent corrosion resistance comprising: a metal substrate;

a film formed on the surface of said metal substrate from a substrate-treating preparation that contains (A) a titanium-containing aqueous liquid obtained by reacting a minimum of one kind of titanium compound selected from a group consisting of hydrolyzable titanium compounds, low condensates of hydrolyzable titanium compounds, titanium hydroxide, and low condensates of titanium hydroxide with aqueous hydrogen peroxide, (B) a minimum of one kind of compound selected from phosphoric acid compounds, metal hydrofluoric acids, and metal fluorides, and (C) an aqueous organic high molecular compound that is stable at pH 7 or lower; and

a finish coating film formed on said substrate-treating film, optionally having an undercoating film formed therebetween.

[Claim 2] A coated steel sheet as stated in Claim 1, wherein the aqueous liquid (A) is a titanium-containing aqueous liquid (A-1) obtained by reacting a hydrolyzable titanium compound and/or a low condensate thereof with aqueous hydrogen peroxide in the presence of a titanium oxide sol.

[Claim 3] A coated steel sheet as stated in Claim 1 or 2, wherein the aqueous liquid (A) is prepared by adding a titanium compound in aqueous hydrogen peroxide.

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[*] Numbers in the margin indicate pagination in the foreign text.

[Claim 4] A coated steel sheet as stated in any one of Claims 1 through 3, wherein the hydrolyzable titanium compounds are titanium monomers that contain groups that are hydrolyzed to hydroxyl groups.

[Claim 5] A coated steel sheet as stated in any one of Claims 1 through 3, wherein the low condensates of hydrolyzable titanium compounds are low condensates of titanium monomers that contain groups that are hydrolyzed to hydroxyl groups.

[Claim 6] A coated steel sheet as stated in any of Claims 1 through 4, wherein the hydrolyzable titanium compounds are represented by General Formula $Ti(OR)_4$ (wherein R's, optionally being the same or different from one another, indicate alkyl groups having from 1 to 5 carbon atoms).

[Claim 7] A coated steel sheet as stated in Claim 1, 2, or 5, wherein the aforesaid low condensates have a degree of condensation of from 2 to 30.

[Claim 8] A coated steel sheet as stated in any one of Claims 1 through 3, wherein the blending proportion of the titanium compounds and aqueous hydrogen peroxide is 0.1 to 100 parts by weight of hydrogen peroxide per 10 parts by weight of the titanium compounds.

[Claim 9] A coated steel sheet as stated in Claim 1, wherein the compound (B) is a minimum of one kind of compound selected from phosphoric acid, metaphosphoric acid, condensed phosphoric acid, condensed metaphosphoric acid, phosphoric acid salts, metaphosphoric acid salts, condensed phosphoric acid salts, condensed metaphosphoric salts, fluorozirconic acid, fluorotitanic acid, hydrofluosilicic acid, fluorozirconates, fluorotitanates, and fluorosilicates.

[Claim 10] A coated steel sheet as stated in Claim 1 or 9, wherein the blending proportion of the compound (B) is from 1 to 400 parts by weight per 100 parts by weight of the solid content of the titanium-containing aqueous liquid (A).

[Claim 11] A coated steel sheet as stated in Claim 1, wherein the aqueous organic high molecular compound (C) is comprised of a minimum of one kind of resin selected from epoxy resins, phenol resins, acrylic resins, urethane resins, polyvinyl alcohol resins, polyalkylene glycol resins, and olefin-carboxylic acid resins.

[Claim 12] A coated steel sheet as stated in Claim 1 or 11, wherein the blending proportion of the aqueous organic high molecular compound (C) is from 10 to 2,000 parts by weight per 100 parts by weight of the solid content of the titanium-containing aqueous liquid (A).

[Claim 13] A coated steel sheet as stated in any one of Claims 1 through 12, wherein the substrate-treating preparation is an aqueous liquid whose pH is from 1 to 7.

[Claim 14] A method for preparing coated steel sheets having excellent corrosion resistance, said method comprising:

applying, onto the surface of a metal substrate, a substrate-treating preparation that contains (A) a titanium-containing aqueous liquid obtained by reacting a minimum of one kind of titanium compound selected from a group consisting of hydrolyzable titanium compounds, low condensates of hydrolyzable titanium compounds, titanium hydroxide, and low condensates of titanium hydroxide with aqueous hydrogen peroxide, (B) a minimum of one kind of compound selected from phosphoric acid compounds, metal hydrofluoric acids, and metal hydrofluorides, and (C) an aqueous organic high molecular compound that is stable at pH 7 or lower so as to form a film having a dry film thickness of from 0.001 to 10 μm;

drying the film; and

subsequently forming a finish coating film on said substrate-treating film, optionally having an undercoating film formed therebetween.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention pertains to coated steel sheets having excellent corrosion resistance that are rendered corrosion resistant with the use of a chromium-free substrate-treating preparation in place of chromating or phosphating.

[0002]

[Prior Art and Problems Thereof] Conventionally, chromating and zinc phosphating are commonly employed for treating the surface of metal substrates, such as cold rolled steel sheets, zinc plated steel sheets, aluminum steel sheets, and so forth. However, the toxicity of chromium now poses a concern. Chromating has various problems, including the problem of sublimation of chromate fume in the treatment process, enormous cost required for wastewater treatment equipment, and problems caused by the elution of chromic acid from chemically converted coatings. Hexavalent chromium compounds are designated as carcinogenic substances by many public organizations, including IARC (International Agency for Research on Cancer Review), and are extremely harmful substances.

[0003] With respect to zinc phosphating, a rinsing process with chromic acid usually follows zinc phosphating; therefore, it has the same problems as chromating. In addition, it has problems related to wastewater processing that is necessitated by the reaction accelerators, metal ions, and so forth contained in zinc-phosphating preparations and sludge-disposal problems caused by the elution of metal ions from the treated metals.

[0004] As treatment methods other than chromating and zinc phosphating, there have been proposed, for instance, (1) a surface treatment method that treats the surface with an aqueous solution that contains aluminum biphosphate and subsequently heats the surface at a temperature of from 150 to 550°C (see JP-B-S53-28857) and (2) a /3 method that treats the surface with an aqueous solution that contains tannic acid (see JP-A-S51-71233). Further, (3) a treatment method that uses sodium nitrite, sodium borate, imidazole, aromatic carboxylic acids, surface active agents, or the like and a treatment method that uses these in combination are practiced.

[0005] However, Method 1 has a problem in that, when a coating material is applied to the thus-treated surface, the coating material does not adhere to the surface sufficiently, and Method 2 has poor corrosion resistance. Method 3, with the use of any of these substances, exhibits poor corrosion resistance in a high-temperature and high-humidity environment.

[0006] In JP-A-S58-224174, JP-A-S60-50179, JP-A-S60-50180, and so forth are disclosed zinc-type steel sheets having a thin film of several micrometers or less in thickness that have a zinc-plated steel sheet as the substrate, a chromate film formed on the substrate, and an organic complex silicate film formed on it as the topmost layer. These are excellent in processability and corrosion resistance. However, because these corrosion-resistant steel sheets have chromate films, they pose the same problems as those described in the foregoing from the aspect of safety and health due to the presence of chromate ions. If these chromate films are eliminated from these corrosion-resistant steel sheets, the resulting steel sheets exhibit insufficient corrosion resistance.

[0007] With respect to phosphating, phosphoric acid compounds that have not been involved in film formation precipitate as sludge and this sludge needs to be disposed of as industrial waste; thus, this treatment requires the implementation of environmental protection measures, waste disposal cost, and so forth.

[0008] The objective of the present invention is to provide coated steel sheets having excellent corrosion resistance that are rendered corrosion resistant with the use of a chromium-free substrate-treating preparation in place of chromating or phosphating.

[0009]

[Means For Solving The Problems] The present inventors learned that coated steel sheets for which is used, as a metal-use corrosion inhibitor, a substrate-treating preparation that is prepared by blending a titanium-containing, specific aqueous liquid; a minimum of one kind of compound selected from phosphoric acid compounds, metal hydrofluoric acids, and metal fluorides; and an aqueous organic high molecular compound achieve the aforesaid objective, thereby attaining the present invention.

[0010] Accordingly, the present invention provides a coated steel sheet having excellent corrosion resistance that comprises a metal substrate; a film formed on the surface of said metal substrate from a substrate-treating preparation that contains (A) a titanium-containing aqueous liquid obtained by reacting a minimum of one kind of titanium compound selected from a group consisting of hydrolyzable titanium compounds, low condensates of hydrolyzable titanium compounds, titanium hydroxide, and low condensates of titanium hydroxide with aqueous hydrogen peroxide, (B) a minimum of one kind of compound selected from phosphoric acid compounds, metal hydrofluoric acids, and metal fluorides, and (C) an aqueous organic high molecular compound that is stable at pH 7 or lower; and a finish coating film formed on said substrate-treating film, optionally having an undercoating film formed therebetween.

[0011]

[Preferred Mode of the Invention] The feature of the coated steel sheets of the present invention is the formation of a substrate-treating film with a specific substrate-treating preparation in place of chromating or phosphating, and highly corrosion-resistant coated steel sheets can be obtained by forming a finish coating film on said substrate-treating film, optionally having an undercoating film therebetween.

[0012] First, the aforesaid substrate-treating preparation will be described.

[0013] Substrate-treating preparation

The substrate-treating preparation used in the present invention contains (A) a titanium-containing aqueous liquid, (B) a minimum of one kind of compound selected from phosphoric acid compounds, metal hydrofluoric acids, and metal fluorides, and (C) an aqueous organic high molecular compound.

[0014] Titanium-containing aqueous liquid (A)

The titanium-containing aqueous liquid (A) used in the substrate-treating preparation is a titanium-containing aqueous liquid that is obtained by reacting a minimum of one kind of titanium compound selected from hydrolyzable titanium compounds, low condensates of hydrolyzable titanium compounds, titanium hydroxide, and low condensates of titanium hydroxide with aqueous hydrogen peroxide. As said aqueous liquid, the present invention can select and use any known liquid as appropriate with no specific limitations as long as it belongs to those described in the foregoing.

[0015] The hydrolyzable titanium compounds described in the foregoing are titanium compounds that have hydrolyzable groups that bond directly to titanium atoms, and they produce titanium hydroxide when react with water, steam, or the like. In the hydrolyzable titanium compounds, all of the groups bonded to the titanium atoms may be hydrolyzable groups, or, alternatively, part of the groups may be previously hydrolyzed to hydroxyl groups.

[0016] The hydrolyzable groups may be any groups that are capable of producing titanium hydroxide by reacting with water, as described in the foregoing. Examples of such groups include lower alkoxyl groups and groups that form salts with titanium atoms [for example, halogen atoms (for example, chlorine atoms and the like), hydrogen atoms, and sulfuric acid ions].

[0017] The hydrolyzable titanium compounds that contain lower alkoxyl groups as the hydrolyzable groups are preferably tetraalkoxytitaniums represented by General Formula $Ti(OR)_4$ (wherein R’s, optionally being the same or different from one another, indicate alkyl groups having from 1 to 5 carbon atoms). Examples of the alkyl groups having from 1 to 5 carbon atoms include a methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, iso-butyl group, sec-butyl group, tert-butyl group, and so forth.

[0018] Typical examples of the hydrolyzable titanium compounds that contain, as the hydrolyzable groups, groups that form salts with titanium atoms include titanium chloride, titanium sulfate, and so forth.

[0019] The low condensates of hydrolyzable titanium compounds are products of a low degree of self-condensation of the aforesaid hydrolyzable titanium compounds. In said low condensates, all of the groups bonded to the titanium atoms may be hydrolyzable groups, or part of the groups may be previously hydrolyzed to hydroxyl groups. /4

[0020] Orthotitanic acid (titanium hydroxide gel) obtained by the reaction of an aqueous solution of titanium chloride, titanium sulfate, or the like with a solution of an alkali, such as ammonia or caustic soda, may also be used as the low condensate.

[0021] The degree of condensation of the aforesaid low condensates of hydrolyzable titanium compounds or low condensates of titanium hydroxide is from 2 to 30, preferably in the range of from 2 to 10. As the aqueous liquid (A), the present invention may use, without any specific limitations, any heretofore-known titanium-containing aqueous liquid obtained by the reaction of the above titanium compounds with aqueous hydrogen peroxide. Specific examples of such aqueous liquids include the following.

[0022] (1) Titanyl ion hydrogen peroxide complex or titanic acid (peroxotitanium hydrate) aqueous solutions that are obtained by adding aqueous hydrogen peroxide to a gel or sol containing titanium hydroxide (see JP-A-S63-35419 and JP-A-H01-224220.)

[0023] (2) Titania film-forming liquids that are synthesized by causing aqueous hydrogen peroxide to act on a titanium hydroxide gel prepared from an aqueous solution of titanium chloride or titanium sulfate and a basic solution (see JP-A-H09-71418 and JP-H10-67516.)

[0024] Furthermore, in the process of preparing the aforesaid titania film-forming liquids, an aqueous solution of titanium chloride or titanium sulfate that have groups that form salts with titanium atoms is reacted with an aqueous solution of an alkali, such as ammonia or caustic soda to precipitate a titanium hydroxide gel, which is called orthotitanic acid. Subsequently, the titanium hydroxide gel is isolated by decantation with the use of water, washed well with water, and combined with aqueous hydrogen peroxide, and excess hydrogen peroxide is decomposed and eliminated; in this manner, a yellow transparent viscous liquid can be obtained.

[0025] The aforesaid precipitated orthotitanic acid is in a polymerized gel state owing to the polymerization of OH’s or hydrogen bonding and, in this state, cannot be used as the titanium-containing aqueous liquid. When aqueous hydrogen peroxide is added to this gel, part of OH’s becomes a peroxidative state and dissolves as peroxotitanic acid ions, or the polymer chains are cleaved into low molecular chains, thereby turning into a kind of sol, and excess hydrogen peroxide decomposes into water and hydrogen; as a consequence, it becomes possible to use this gel as the titanium-containing aqueous liquid for forming inorganic film.

[0026] Because this sol contains only oxygen atoms and hydrogen atoms besides titanium atoms, water and oxygen alone are generated when the sol is converted into titanium oxide by drying or firing; therefore, unlike sol-gel methods or heat decomposition of sulfates or the like, it is not required to eliminate carbon components or halogen components, and it is possible to form crystalline titanium oxide film having a relatively high density even at a temperature lower than in the prior art.

[0027] (3) Titanium oxide-forming solutions obtained by adding aqueous hydrogen peroxide to an aqueous solution of an inorganic titanium compound, such as titanium chloride or titanium sulfate, thereby forming a peroxotitanium hydrate; adding a basic substance to this hydrate; leaving the resulting solution standing or heating it, thereby precipitating a peroxotitanium hydrate polymer; subsequently removing the dissolved components, other than water, derived from at least the titanium-containing raw material solution; and further causing hydrogen peroxide to act on the precipitate (see JP-A-2000-247638 and JP-A-2000-247639.)

[0028] As the aqueous liquid (A), the present invention may use any titanium-containing aqueous liquids obtained by the aforesaid known methods, and, furthermore, it may use a titanium-containing aqueous liquid obtained by a method that adds a titanium compound in aqueous hydrogen peroxide. As said titanium compound, it is preferable to use hydrolyzable titanium compounds represented by the aforesaid General Formula $Ti(OR)_4$ (wherein R's, optionally being the same or different from one another, indicate alkyl groups having from 1 to 5 carbon atoms), which contain groups that are hydrolyzed to give hydroxyl groups, or low condensates of these hydrolyzable titanium compounds.

[0029] The blending proportion of the hydrolyzable titanium compound and/or its low condensate (hereinafter these are referred to simply as "hydrolyzable titanium compound a") and aqueous hydrogen peroxide is preferably within the range of from 0.1 to 100 parts by weight, better yet, from 1 to 20 parts by weight, in terms of hydrogen peroxide, per 10 parts of hydrolyzable titanium compound a. A proportion of less than 0.1 part by weight of aqueous hydrogen peroxide in terms of hydrogen peroxide will result in insufficient chelate formation and produce opaque precipitates. On the other hand, if the proportion exceeds 100 parts by weight, part of hydrogen peroxide remains unreacted and emits hazardous active oxygen during storage; thus, this range is not desirable.

[0030] The hydrogen peroxide concentration in the aqueous hydrogen peroxide is not specifically limited, but it is preferably in the range of from 3 to 30% by weight from the viewpoint of ease of handling and the solid content of the formed liquid, which influences ease of coating operation.

[0031] The aqueous liquid (A) obtained with the use of hydrolyzable titanium compound a is produced by reacting hydrolyzable titanium compound a with aqueous hydrogen peroxide at a temperature range of from 1 to 70°C for 10 minutes to 20 hours.

[0032] In the process of forming the aqueous liquid (A) with the use of hydrolyzable titanium compound a, it is conjectured that, when hydrolyzable titanium compound a is reacted with aqueous hydrogen peroxide, the hydrolyzable titanium compound is hydrolyzed with water, thereby forming a hydroxyl-containing titanium compound, and, immediately thereafter, hydrogen peroxide coordinates to the formed hydroxyl-containing titanium compound. The aqueous liquid can be obtained owing to the nearly concurrent occurrence of this hydrolysis reaction and the coordination of hydrogen peroxide. This process produces a chelate liquid that is highly stable at room temperature and that can endure long-term storage. Titanium hydroxide gels used in conventional production methods are partially three-dimensional owing to Ti-O-Ti bonding, and these gels are essentially different from the reaction product with aqueous hydrogen peroxide with respect to the composition and stability.

[0033] Subjecting the aqueous liquid (A) comprised of hydrolyzable titanium compound a to a heat treatment or autoclave treatment at 80°C or higher yields a titanium oxide dispersion that

contains ultrafine crystallized titanium oxide particles. If the temperature is below 80°C, the crystallization of titanium oxide does not progress sufficiently. The titanium oxide dispersion thus prepared contains ultrafine titanium oxide particles having a particle size of 10 nm or smaller, preferably in the range of from 1 nm to 6 nm. The /5
appearance of said dispersion is semitransparent. If said particle size is larger than 10 nm, the film-forming property of the dispersion deteriorates (a film of 1 µm or thicker develops cracks), thus rendering this range undesirable. This dispersion can also be used in the present invention.

[0034] The aqueous liquid (A) comprised of hydrolyzable titanium compound a can, by itself, form dense titanium oxide film having an excellent adhesion property when it is applied to a steel sheet material and dried or heated at a low temperature.

[0035] The temperature of the heat treatment to form titanium oxide film is preferably 200°C or lower, better yet, 150°C or lower.

[0036] The aqueous liquid (A) comprised of hydrolyzable titanium compound a forms amorphous titanium oxide film that contains some hydroxyl groups when heat-treated at the aforesaid temperature range.

[0037] On the other hand, the titanium oxide dispersion obtained as a result of the heat treatment at 80°C or higher can form crystalline titanium oxide film simply by applying it to a substrate; therefore, it is useful as a coating material for substrate materials that cannot be heat-treated.

[0038] As the aqueous liquid (A), the present invention may also use a titanium-containing aqueous liquid [hereinafter referred to as (A-1)] that is obtained by reacting, in the presence of a titanium oxide sol, the above-mentioned hydrolyzable titanium compound and/or low condensate of the hydrolyzable titanium compound with aqueous hydrogen peroxide. As said hydrolyzable titanium compound and/or low condensate of the hydrolyzable titanium compound (hydrolyzable titanium compound a), it is preferable to use titanium monomers represented by the aforesaid General Formula $Ti(OR)_4$ (wherein R’s, optionally being the same or different from one another, indicate alkyl groups having from 1 to 5 carbon atoms), which contain groups that are hydrolyzed to give hydroxyl groups, or low condensates of these hydrolyzable titanium compounds.

[0039] The aforesaid titanium oxide sol is a sol in which amorphous titania or anatase titania particles are dispersed in water (which may contain, as necessary, for example, aqueous organic solvents, such as alcohols, alcohol ethers, or the like.)

[0040] As the aforesaid titanium oxide sol, the present invention may use those that have been known heretofore. Examples of said titanium oxide sol that can be used here include: (1) sols that are obtained by hydrolyzing titanium-containing solutions, such as titanium sulfate, titanyl sulfate, and the like; (2) sols that are obtained by hydrolyzing organic titanium compounds, such as titanium alkoxides and the like; and (3) amorphous titania sols that are obtained by dispersing in water titanium oxide agglomerates that are obtained, for example, by the hydrolysis or neutralization of a solution of titanium halide, such as titanium tetrachloride or the like, or sols that are obtained by firing said titanium oxide agglomerates to form them into anatase titanium fine particles and then dispersing them in water. Firing amorphous titania at a temperature that is at least higher than anatase crystallization temperature--for example, a temperature of from 400°C to 500°C or higher--can convert amorphous titania to anatase titania. Examples of said titanium oxide aqueous sols include “TKS-201” (a product name, manufactured by TEICA Co., anatase type crystal form, average particle size: 6 nm), “TA-15” (a product name, manufactured by Nissan Chemical Co., anatase type crystal form), and “STS-11” (a product name, manufactured by Ishihara Sangyo Co., anatase type crystal form).

[0041] The weight ratio of the aforesaid titanium oxide sol and titanium-hydrogen peroxide reaction product in the case of using the sol in the reaction of hydrolyzable titanium compound a and aqueous hydrogen peroxide is in the range of from 1/99 to 99/1, preferably from about 10/90 to 90/10. When the weight ratio is less than 1/99, the resulting aqueous liquid does not show the addition effects of titanium oxide sol, such as stability, photoreactivity, and the like, while a ratio exceeding 99/1 leads to deterioration of the film-forming property and, therefore, is not desirable.

[0042] The blending proportion of hydrolyzable titanium compound a and aqueous hydrogen peroxide is preferably within the range of from 0.1 to 100 parts by weight, better yet, from 1 to 20 parts by weight, in terms of hydrogen peroxide, per 10 parts of hydrolyzable titanium compound a. A proportion of less than 0.1 part by weight of aqueous hydrogen peroxide in terms of hydrogen peroxide will result in insufficient chelate formation and produce opaque precipitates. On the other hand, if the proportion exceeds 100 parts by weight, part of hydrogen peroxide remains unreacted and emits hazardous active oxygen during storage; thus, this range is not desirable.

[0043] The hydrogen peroxide concentration in the aqueous hydrogen peroxide is not specifically limited, but it is preferably in the range of from 3 to 30% by weight from the viewpoint of ease of handling and the solid content of the formed liquid, which influences ease of coating operation.

[0044] The aqueous liquid (A-1) is produced by reacting hydrolyzable titanium compound a with aqueous hydrogen peroxide at a temperature range of from 1 to 70°C for 10 minutes to 20 hours in the presence of a titanium oxide sol.

[0045] In the process of forming the aqueous liquid (A-1), it is conjectured that, when hydrolyzable titanium compound a is reacted with aqueous hydrogen peroxide, the hydrolyzable titanium compound is hydrolyzed with water, thereby forming a hydroxyl-containing titanium compound, and, immediately thereafter, hydrogen peroxide coordinates to the formed hydroxyl-containing titanium compound. The aqueous liquid can be obtained owing to the nearly concurrent occurrence of this hydrolysis reaction and the coordination of hydrogen peroxide. This process produces a chelate liquid that is highly stable at room temperature and that can endure long-term storage. Titanium hydroxide gels used in conventional production methods are partially three-dimensional owing to Ti-O-Ti bonding, and these gels are essentially different from the reaction product with aqueous hydrogen peroxide with respect to the composition and stability. Furthermore, the use of titanium oxide sol prevents a partial condensation reaction from occurring in the synthesis process, thus preventing the resulting liquid from thickening. The reason for this, it is conjectured, is that the condensation reaction products are adsorbed to the surface of the titanium oxide sol, thereby preventing polymerization in the solution state.

[0046] Subjecting the titanium-containing aqueous liquid (A-1) to a heat treatment or autoclave treatment at 80°C or higher yields a titanium oxide dispersion that contains ultrafine crystallized titanium oxide particles. If the temperature is below 80°C, the crystallization of titanium oxide does not progress sufficiently. The titanium oxide dispersion thus prepared contains ultrafine titanium oxide particles having a particle size of 10 nm or smaller, preferably in the range of from 1 nm to 6 nm. The appearance of said dispersion /6 is semitransparent. The appearance of said dispersion is semitransparent. If said particle size is larger than 10 nm, the film-forming property of the dispersion deteriorates (a film of 1 μm or thicker develops cracks), thus rendering this range undesirable. This dispersion can also be used in the present invention.

[0047] The titanium-containing aqueous liquid (A-1) can, by itself, form dense titanium oxide film having an excellent adhesion property when it is applied to a steel sheet material and dried or heated at a low temperature.

[0048] The temperature of the heat treatment to form titanium oxide film is preferably 200°C or lower, better yet, 150°C or lower.

[0049] The titanium-containing aqueous liquid (A-1) forms anatase-type titanium oxide film that contains some hydroxyl groups when heat-treated at the aforesaid temperature range.

[0050] As the aqueous liquid (A) of the present invention, it is especially desirable to use the aforesaid aqueous liquid obtained with the use of hydrolyzable titanium compound a and the aqueous solution (A-1) because they are excellent in storage stability, corrosion resistance, and so forth.

[0051] To the aforesaid titanium-containing aqueous liquid (A), other pigments and sols may be further added and dispersed as necessary. Examples of the additives include commercially available titanium oxide sols, titanium oxide powders, mica, talc, silica, baryta, clay, and so forth.

[0052] Compound (B)

The compound that comprises component (B) of the substrate-treating preparation is a minimum of one kind of compound selected from phosphoric acid compounds, metal hydrofluoric acids, and metal fluorides.

[0053] Examples of the aforesaid phosphoric acid compounds include monophosphoric acids, such as phosphorous acid, strong phosphoric acid, triphosphoric acid, hypophosphorous acid, hypophosphoric acid, trimetaphosphoric acid, diphosphorous acid, diphosphoric acid, pyrophosphorous acid, pyrophosphoric acid, metaphosphorous acid, metaphosphoric acid, phosphoric acid (orthophosphoric acid), phosphoric acid derivatives, and the like, and salts thereof and condensed phosphoric acids, such as tripolyphosphoric acid, tetraphosphoric acid, hexaphosphoric acid, condensed phosphoric acid derivatives, and the like, and salts thereof. These compounds can be used either singly or in combination of two or more kinds. Further, examples of alkali compounds that form the aforesaid salts include organic or inorganic alkali compounds containing lithium, sodium, potassium, ammonium, or the like. As the phosphoric acid compounds, it is preferable to use those that are soluble in water.

[0054] The use of sodium pyrophosphate, sodium tripolyphosphate, sodium tetraphosphate, metaphosphoric acid, ammonium metaphosphate, sodium hexametaphosphate, or the like as the phosphoric acid compound is particularly desirable because these phosphoric acid compounds remarkably improve the storage stability of the resulting coating preparation, the corrosion resistance of the resulting film, and so forth.

[0055] In the present invention, a blended product of the titanium-containing aqueous liquid (A) and the phosphoric acid compound is believed to form a complex structure between them because the acidic phosphate ion that bonds with said phosphoric acid compound coordinates to the titanium ion.

[0056] Such a reaction can be readily brought about by simply mixing both components. For example, it can be accomplished by leaving the mixture standing at room temperature (20°C) for about 5 minutes to about 1 hour or, in the case of forcefully overheating [sic] the mixture, by heating it, for example, at about 30 to about 70°C for from about 1 minute to about 30 minutes.

[0057] Examples of the aforesaid metal hydrofluoric acids and metal fluorides include fluorozirconic acid, fluorotitanic acid, hydrofluosilicic acid, fluorozirconates, fluorotitanates, fluorosilicates, and so forth. Examples of the substances that form salts of the metal hydrofluoric acids include sodium, potassium, lithium, ammonium, and so forth, of which potassium and sodium are desirable. Concrete examples include potassium fluorozirconate, sodium fluorotitanate, sodium fluorosilicate, potassium fluorosilicate, and so forth.

[0058] The phosphoric acid compounds, metal hydrofluoric acids, and metal fluorides may be used singly or in combination of two or more kinds. The blending proportion of the compound (B) is preferably in the range of from 1 to 400 parts by weight, better yet, from 10 to 200 parts by weight, per 100 parts by weight of the solid content of the titanium-containing aqueous liquid (A).

[0059] Aqueous organic high molecular compound (C)

The substrate-treating preparation further incorporates an aqueous organic high molecular compound (C) besides the aforesaid components. As the aqueous organic high molecular compound (C), the present invention can use any known aqueous liquid of an organic high molecular compound (C) that, in itself, is highly stable at pH 7 or lower, without posing any possibility that their organic resin components that are dissolved or dispersed in water agglomerate and precipitate or give rise to thickening or gelling problems.

[0060] The aqueous organic high molecular compound (C) may be in the form of an aqueous solution, an aqueous dispersion, or an emulsion. The organic high molecular compounds can be dissolved, dispersed, or emulsified in water by known methods. More specifically, as the organic high molecular compound, the present invention may use compounds having functional groups [for example, a minimum of one kind of group, such as a hydroxyl group, carboxyl group, amino (imino) group, sulfide group, phosphine group, and the like] that are by themselves soluble or dispersible in water. The present invention may also use such compounds in which part or all of the functional groups have been neutralized as necessary with, when the compounds are acidic resins (such as carboxyl group-containing resins and the like), an amine compound, such as ethanolamine, triethylamine, or the like; aqueous ammonia; an alkali metal hydroxide, such as lithium hydroxide, sodium hydroxide, potassium hydroxide, or the like, and, when the compounds are basic resins (such as amino group-containing resins), with a fatty acid, such as acetic acid, lactic acid, or the like; a mineral acid, such as phosphoric acid or the like; and so forth.

[0061] Examples of such an aqueous organic high molecular
compound (C) include epoxy resins, phenol resins, acrylic resins, /7
urethane resins, olefin-carboxylic acid resins, nylon resins, polyoxyalkylene chain-containing resins, polyvinyl alcohol, polyglycerol, carboxymethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, and the like.

[0062] Suitable as the aforesaid epoxy resins are cationic epoxy resins obtained by the addition of amine to epoxy resins; modified epoxy resins, such as acrylic-modified epoxy resins, urethane-modified epoxy resins, and the like; and so forth. Examples of the cationic epoxy resins include adducts of epoxy compounds with primary mono- or poly-amines, secondary mono- or poly-amines, mixtures of primary and secondary poly-amines (see, for example, U.S. Pat. No. 3,984,299); adducts of epoxy compounds with secondary mono- or poly-amines having ketiminized primary amino groups (see, for example, U.S. Pat. No.

4,017,438); etherification reaction products of epoxy compounds with hydroxyl compounds having ketiminized primary amino groups (see, for example, JP-A-S59-43013); and so forth.

[0063] It is preferable for the aforesaid epoxy compounds to have a number average molecular weight of from 400 to 4,000, better yet, from 800 to 2,000, and an epoxy equivalent of from 190 to 2,000, better yet, from 400 to 1,000. Such epoxy compounds can be obtained by, for example, the reaction of polyphenol compounds with epichlorohydrin. Examples of the polyphenol compounds include bis(4-hydroxyphenyl)-2,2-propane, 4,4-dihydroxybenzophenone, bis(4-hydroxyphenyl)-1,1-ethane, bis(4-hydroxyphenyl)-1,1-isobutane, bis(4-hydroxy-tert-butylphenyl)-2,2-propane, bis(2-hydroxynaphthyl)methane, 1,5-dihydroxynaphthalene, bis(2,4-dihydroxyphenyl)methane, tetra(4-hydroxyphenyl)-1,1,2,2-ethane, 4,4-dihydroxydiphenyl sulfone, phenol novolac, cresol novolac, and the like.

[0064] Preferably used as the aforesaid phenol resins are those prepared by dissolving in water high molecular compounds that are obtained by heating phenol components and formaldehydes in the presence of reaction catalysts and thereby subjecting them to addition polycondensation. As the aforesaid phenol components, which are a starting material, bifunctional phenol compounds, trifunctional phenol compounds, tetra- or higher functional phenol compounds, and the like can be used. Examples of bifunctional phenol compounds include o-cresol, p-cresol, p-tert-butylphenol, p-ethyl phenol, 2,3-xylenol, 2,5-xylenol, and the like. Examples of trifunctional phenol compounds include phenol, m-cresol, m-ethylphenol, 3,5-xylenol, m-methoxyphenol, and the like. Examples of tetrafunctional phenol compounds include bisphenol A, bisphenol F, and the like. These phenol compounds may be used either singly or in combination of two or more kinds.

[0065] Examples of the aforesaid acrylic resins include, for example, homopolymers or copolymers of monomers having hydrophilic groups, such as carboxyl, amino, or hydroxyl groups; copolymers of hydrophilic group-containing monomers with other copolymerizable monomers; and the like. These resins are obtained by emulsion polymerization, suspension polymerization, or solution polymerization, which is optionally followed by neutralization for conversion to aqueous resins. The resulting resins may be further modified, if required.

[0066] Examples of the aforesaid carboxyl-containing monomers include acrylic acid, methacrylic acid, maleic acid, maleic anhydride, crotonic acid, itaconic acid, and so forth.

[0067] Examples of the nitrogen-containing monomers include nitrogen-containing alkyl (meth)acrylates, such as N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N-t-butylaminoethyl (meth)acrylate, and the like; polymerizable amides, such as acrylamide, methacrylamide, N-methyl (meth)acrylamide, N-ethyl (meth)acrylamide, N-methylol (meth)acrylamide, N-methoxymethyl (meth)acrylamide, N-butoxymethyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide, N,N-dimethylaminoethyl (meth)acrylamide, and the like; nitrogen-containing aromatic monomers, such as 2-vinylpyridine, 1-vinyl-2-pyrrolidone, 4-vinylpyridine, and the like; allyl amines; and so forth.

[0068] Examples of the hydroxyl-containing monomers include monoesters of polyhydric alcohols with acrylic acid or methacrylic acid, such as 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, 2,3-dihydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, and the like; compounds obtained by subjecting the aforesaid monoesters of polyhydric alcohols and acrylic acid or methacrylic acid to ring-opening polymerization with ε-caprolactone; and so forth.

[0069] Other polymerizable monomers include alkyl (meth)acrylates having 1 to 24 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl acrylate, n-octyl (meth)acrylate, lauryl (meth)acrylate, tridecyl (meth)acrylate, octadecyl (meth)acrylate, isostearyl (meth)acrylate, and the like; styrene; vinyl acetate; and /8 the like. These compounds may be used either singly or in combination of two or more kinds. As used herein, the term "(meth)acrylate" is intended to mean acrylate or methacrylate.

[0070] Preferred urethane resins include those prepared by subjecting polyurethanes that are prepared from polyols (such as polyester polyols, polyether polyols, and the like) and diisocyanate to chain extension optionally in the presence of, as a chain extender, a low molecular compound having a minimum of two active hydrogen atoms, such as diol or diamine, and then by dispersing or dissolving the urethane resins stably in water. Such urethane resins can be selected from a wide range of known urethane resins (see, for example, JP-B-S42-24192, JP-B-S42-24194, JP-B-S42-5118, JP-B-S49-986, JP-B-S49-33104, JP-B-S50-15027, and JP-B53-29175.) The polyurethane resins can be dispersed or dissolved stably in water by, for example, the following methods.

[0071] (1) A method that introduces an ionic group, such as a hydroxyl group, amino group, or carboxyl group, into the side chain or the terminal of a polyurethane polymer so as to impart hydrophilicity to the polymer and disperses or dissolves the polymer in water by self-emulsification.

[0072] (2) A method according to which a polyurethane polymer that has completed the reaction or a polyurethane polymer whose terminal isocyanate group is blocked with a blocking agent, such as an oxime, alcohol, phenol, mercaptan, amine, sodium bisulfite, or the like, is dispersed forcibly in water with the use of an emulsifier and mechanical shear force. A method that combines an isocyanate-terminated polyurethane polymer with water, an emulsifier, and a chain extender and, using a mechanical shear force, concurrently performs the dispersion of the polymer and the conversion of the polymer into a higher molecular polymer.

[0073] (3) A method that obtains a water-soluble polyurethane resin with the use of a water-soluble polyol, such as polyethylene glycol or the like, as the main starting-material polyol of the polyurethane and disperses or dissolves this polyurethane in water.

[0074] As the aforesaid polyurethane resins, the dispersions or solutions of the aforesaid polyurethane resins prepared by the above methods can be used either singly or in combination.

[0075] Examples of the diisocyanate that can be used for the synthesis of the aforesaid polyurethane resins include aromatic, alicyclic, and aliphatic diisocyanates. Concrete examples of these diisocyanates include hexamethylene diisocyanate, tetramethylene diisocyanate, 3,3′-dimethoxy-4,4′-biphenylene diisocyanate, p-xylylene diisocyanate, m-xylylene diisocyanate, 1,3-(diisocyanatomethyl) cyclohexanone, 1,4-(diisocyanatomethyl) cyclohexanone, 4,4′-diisocyanatocyclohexanone, 4,4′-methylene bis(cyclohexyl isocyanate), isophorone diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, p-phenylene diisocyanate, diphenylmethane diisocyanate, m-phenylene diisocyanate, 2,4-naphthalene diisocyanate, 3,3′-dimethyl-4,4′-biphenylene diisocyanate, 4,4′-biphenylene diisocyanate, and the like. Of these, particularly preferred are 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, hexamethylene diisocyanate, and isophorone diisocyanate.

[0076] Commercial products of the aforesaid polyurethane resins include “Hydran HW-330,” “Hydran HW-340,” and “Hydran HW-350” (all of which are products of Dainippon Ink and Chemicals, Inc.), “Superflex 100,” “Superflex 150,” and “Superflex F-3438D” (all of which are products of Dai-Ichi Kogyo Seiyaku Co.), and so forth.

[0077] Preferable as the aforesaid polyvinyl alcohol resins are those having a saponification degree of not lower than 87%, in particular, those having a saponification degree of not lower than 98%, which are called completely saponified polyvinyl alcohols. Further, the resins preferably have a number average molecular weight of 3,000 to 100,000.

[0078] Preferably used as the aforesaid polyoxyalkylene chain-containing resins are resins that contain polyoxyethylene chains or polyoxypropylene chains. Examples of such resins include polyethylene glycol, polypropylene glycol, blocked polyoxyalkylene glycol in which the aforesaid polyoxyethylene chains and polyoxypropylene chains are bonded in a block shape, and so forth.

[0079] As the aforesaid olefin-carboxylic acid resins can be used a minimum of one kind of water-dispersible or water-soluble resin selected from the following two kinds: (1) copolymers of olefins, such as ethylene, propylene, and the like, and polymerizable unsaturated carboxylic acids and (2) resins that are obtained by adding a polymerizable unsaturated compound to a dispersion of the above copolymer to effect emulsion polymerization and subsequently by performing intraparticle [sic] crosslinking.

[0080] The aforesaid copolymers (1) are copolymers comprised of one or more kinds of olefins and one or more kinds of unsaturated carboxylic acids, such as (meth)acrylic acid, maleic acid, and the like. In the aforesaid copolymers (1), the content of said unsaturated carboxylic acid is preferably in the range of from 3 to 60% by weight, better yet, from 5 to 40% by weight, and the copolymers can be dispersed in water by neutralizing the acid groups in the copolymers with a basic substance.

[0081] The aforesaid resins (2) are crosslinked resins that are obtained by adding a polymerizable unsaturated compound to an aqueous dispersion of the above copolymer (1) to effect emulsion polymerization and subsequently by performing intraparticle [sic] crosslinking. Examples of said polymerizable unsaturated compound include the vinyl monomers that are listed earlier in the description of the water-dispersible or water-soluble acrylic resins, and these vinyl monomers may be selected as appropriate and used either singly or in combination of two or more kinds.

[0082] The blending proportion of the aqueous organic high molecular compound (C) is preferably from 10 to 2,000 parts by weight, better yet, from 100 to 1,000 parts by weight, per 100 parts by weight of the solid content of the titanium-containing aqueous liquid (A) for /9 better stability, corrosion resistance, and the like of the liquid.

[0083] Because the substrate-treating preparation becomes a stable liquid in a neutral or acidic region, its pH is preferably in the range of from 1 to 7, better yet, from 1 to 5.

[0084] In addition to the aforesaid components, the substrate-treating preparation may further contain, if necessary, thickeners, surface active agents, antimicrobial agents, rust-preventive agents (such as tannic acid, phytic acid, benzotriazole, and the like), and pigments, such as coloring pigments, extender pigments, rust-preventive pigments, and so forth.

[0085] The substrate-treating preparation may be diluted as necessary for use with a hydrophilic solvent, such as methanol, ethanol, isopropyl alcohol, ethylene glycol, propylene glycol, or the like.

[0086] The following will explain in detail the coated steel sheets of the present invention.

[0087] Coated steel sheets

Examples of the metal substrate used for the coated steel sheets of the present invention include, but are not limited to, cold-rolled steel sheets, hot dip galvanized steel sheets, electrogalvanized steel sheets, iron-zinc alloy plated steel sheets, nickel-zinc alloy plated steel sheets, aluminum-zinc alloy plated steel sheets (for example, alloy-plated steel sheets that are sold under such product names as "Galvalium" or "Galfan"), aluminum plated steel sheets, aluminum sheets, and so forth. It is usually preferable for the metal substrate used here to be untreated, but the use of metal substrates that have been subjected to a chemical conversion treatment, such as chromating, zinc phosphating, or composite oxide film treatment does not pose any problems.

[0088] The aforesaid substrate-treating preparation is applied to the surface of the aforesaid metal substrate and dried, thereby forming a surface-treating film.

[0089] The substrate-treating preparation can be applied to a metal substrate material (which may be assembled objects) by any known coating method, such as dip coating, shower coating, spray coating, roll coating, and electrodeposition coating. As for the drying condition of the substrate-treating preparation, it is preferable to dry it for about 2 seconds to about 30 minutes under such conditions that attain a peak metal temperature of about 60 to 250°C.

[0090] Furthermore, it is preferable for the dried film thickness of the substrate-treating preparation to be usually in the range of from 0.001 to 10 µm, better yet, from 0.1 to 3 µm. A thickness that is less than 0.001 µm leads to poor corrosion resistance, water resistance, and the like, while a thickness exceeding 10 µm leads to cracking of the surface-treating film, deterioration of processability, and so forth, thus rendering these ranges undesirable.

[0091] On the aforesaid surface-treating film, a finish coating film is formed, with or without an undercoating film therebetween. The types of the undercoating and finish coating used here are not specifically limited and may be selected as appropriate according to the objective. Coating compositions are classified, for example, into solvent-based coating materials, water-based coating materials, coating powder materials, and so forth based on their forms; into baking-curable coating materials, light-curable coating materials, room-temperature drying coating materials, and so forth based on their curing methods, and into coloring coating materials, metallic coating materials, clear coating materials, and so forth based on the appearance of the films obtained by applying and drying coating compositions. The present invention may use any of these types.

[0092] The finish coating film may be a one-coat/one-bake type, but two-coat/one-bake, two-coat/two-bake, three-coat/one-bake, or other known systems may also be used, and it is also possible to form the finish coating film on the undercoating film via an intermediate coating film formed therebetween.

[0093] Besides ordinary finish coating materials that are usually applied to achieve good appearance, it is possible to apply organic covering agents having functionalities, such as lubricity, fingerprint resistance, and the like as the finishing coat.

[0094] The coated steel sheets of the present invention can be used, without any specific limitations, for building materials, household appliances, automobiles, cans, and any other applications in which coated steel sheets are conventionally used, and the coating method of the undercoating material and finish coating material should be selected as appropriate according to the use of the sheets, the shape of the object to be coated, and so forth. For example, in the case of coating a formed product, spray coating, brush coating, electrodeposition coating, and the like are suitable. In the case of coating sheet-form products, such as precoated steel sheets or the like, roll coating, curtain flow coating, and the like are ideal.

[0095]

[Effects of the Invention] Because the present invention has the aforesaid constitution, it is believed to yield the following effect.

[0096] According to the present invention, it is conjectured that, when a substrate-treating preparation having the aforesaid constitution is applied to a metal substrate, such as a steel sheet or the like, and heated to form a substrate-treating film, phosphoric acid compounds, metal hydrofluoric acids, metal fluorides, and the like, which are a component (B) that constitutes the substrate-treating preparation, function as an etching agent for the metal, while the titanium-containing aqueous liquid (A) and aqueous organic high molecular compound (C) form a film that has excellent adhesion to the substrate and also has low oxygen permeability and steam permeability. As a consequence, a coated steel sheet having extremely high corrosion resistance and durability can be obtained.

[0097]

[Working Examples] The following will explain the present invention in further detail by presenting working examples and comparative examples. In the following, "parts" and "%" each mean "parts by weight" and "% by weight." The present invention is not limited to or restricted by the following working examples.

[0098] Preparation of titanium-containing aqueous liquid

Preparation Example 1

Aqueous ammonia (1:9) was added drop by drop to 500 cc of an aqueous solution obtained by diluting 5 cc of a 60% titanium tetrachloride solution with distilled water, thereby precipitating titanium hydroxide. The precipitate was washed with distilled water, combined with 10 cc of a 30% solution of aqueous hydrogen peroxide and stirred, thereby obtaining a yellow, translucent, and viscous titanium-containing aqueous liquid (A1) having a solid content of 2%.

[0099] Preparation Example 2

A mixture of 10 parts of tetraisopropoxy titanium and 10 parts of isopropanol was added drop by drop to a mixture of 10 parts of 30% aqueous hydrogen peroxide and 100 parts of deionized water at 20°C over the course of 1 hour while the resulting mixture was stirred. Thereafter, the resulting mixture was aged at 25°C for 2 hours, thereby obtaining a yellow, transparent, and slightly viscous titanium-containing aqueous liquid (A2) having a solid content of 2%. /10

[0100] Preparation Example 3

The procedure for producing titanium-containing aqueous liquid (A2) was repeated under the same preparation conditions, except that tetra-n-butoxy titanium was used in place of tetraisopropoxy titanium, thereby obtaining a titanium-containing aqueous liquid (A3) having a solid content of 2%.

[0101] Preparation Example 4

The procedure for producing titanium-containing aqueous liquid (A2) was repeated under the same preparation conditions, except that a trimer of tetraisopropoxy titanium was used in place of tetraisopropoxy titanium, thereby obtaining a titanium-containing aqueous liquid (A4) having a solid content of 2%.

[0102] Preparation Example 5

The procedure for producing titanium-containing aqueous liquid (A2) was repeated, except that 3 times the amount of aqueous hydrogen peroxide was added drop by drop at 50°C over the course of 1 hour and that the subsequent aging was carried out at 60°C for 3 hours, thereby obtaining a titanium-containing aqueous liquid (A5) having a solid content of 2%.

[0103] Preparation Example 6

Titanium-containing aqueous liquid A3 was heated at 95°C for 6 hours, thereby obtaining a whitish yellow translucent titanium-containing aqueous liquid (6A) having a solid content of 2%.

[0104] Preparation Example 7

A mixture of 10 parts of tetraisopropoxy titanium and 10 parts of isopropanol was added drop by drop to a mixture of 5 parts (in terms of solid content) of TKS-203 (a titanium oxide sol, a product of TEICA Co.), 10 parts of 30% aqueous hydrogen peroxide, and 100 parts of deionized water at 10°C over the course of 1 hour while the resulting mixture was stirred. Thereafter, the resulting mixture was aged at 10°C for 24 hours, thereby obtaining a yellow, transparent, and slightly viscous titanium-containing aqueous liquid (A7) having a solid content of 2%.

[0105] Preparation of acrylic resin

Preparation Example 8

In a 1 liter-capacity four-neck flask equipped with a thermometer, stirrer, condenser, and dropping funnel was placed 180 parts of isopropyl alcohol, and the flask was purged with nitrogen, after which the temperature inside the flask was adjusted to 85°C. Into this flask was added drop by drop over the course of about 2 hours a monomer mixture consisting of 140 parts of ethyl acrylate, 68 parts of methyl methacrylate, 15 parts of styrene, 15 parts of N-n-butoxymethyl acrylamide, 38 parts of 2-hydroxyethyl acrylate, and 24 parts of acrylic acid, together with 6 parts of 2,2′-azobis(2,4-dimethylvaleronitrile) as a catalyst. After the addition was completed, the reaction was continued at the same temperature for 5 more hours. As a result, a colorless transparent resin solution was obtained that had a polymerization degree of nearly 100%, a solid content of about

63%, and an acid value of about 67. This resin solution (500 parts) was mixed with 108 parts of dimethylaminoethanol. After water was added to this mixture, the mixture was thoroughly stirred, thereby obtaining an aqueous acrylic resin dispersion (C1) having a solid content of 30%.

[0106] Preparation of amine-modified epoxy resin

Preparation Example 9

Into a reactor equipped with a stirrer, reflux condenser, thermometer, and liquid dropper were charged 1,880 g (0.5 mole) of "Epikote 1009" resin (an epoxy resin manufactured by Shell Chemical Co., molecular weight: 3,750) and 1,000 g of a mixed solvent (methyl isobutyl ketone/xylene=1/1 in weight ratio). The solution was then cooled to 70°C, and 70 g of di(n-propanol)amine that had been weighed into the liquid dropper was added to the solution drop by drop over the course of 30 minutes. During this addition, the reaction temperature was kept at 70°C. After this addition was completed, the reaction mixture was maintained at 120°C for 2 hours to allow the reaction to complete, thereby obtaining an amine-modified epoxy resin having a solid content of 66%. Twenty-five parts of 88% formic acid was added per 1,000 g of the obtained resin. After water was added to this mixture, the mixture was thoroughly stirred, thereby obtaining an aqueous amine-modified epoxy resin dispersion (C2) having a solid content of 30%.

[0107] Preparation of substrate-treating preparation

Substrate-treating preparation S1 (for working-example use)

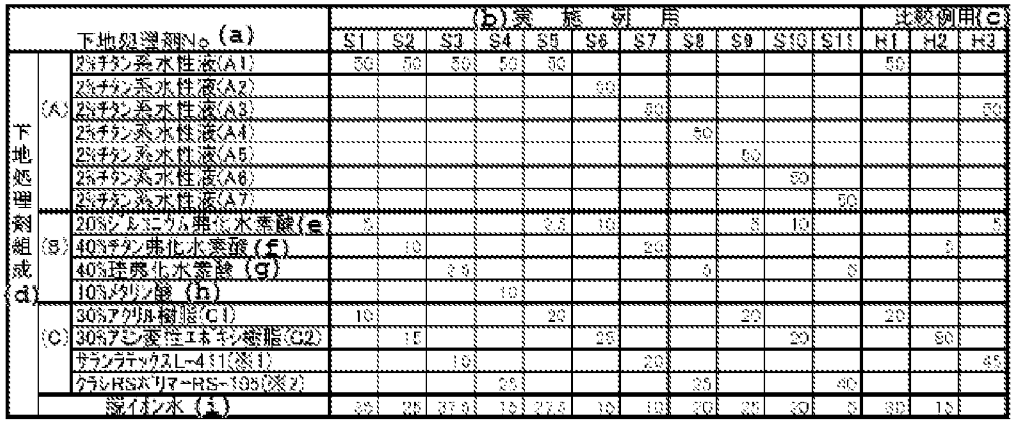
Substrate-treating preparation S1 was obtained by mixing 50 parts of 2% titanium-containing aqueous liquid (A1), 5 parts of 20% fluorozirconic acid, 10 parts of 30% acrylic resin aqueous dispersion (C1), and 35 parts of deionized water.

[0108] Substrate-treating preparations S2 through S11 (for working-example use) and substrate-treating preparations H1 through H3 (for comparative-example use) using the components shown in Table 1, substrate-treating preparations were prepared in the same manner as the aforesaid substrate-treating preparation S1.

[0109]

[Table 1]

TABLE 1: PREPARATION OF SUBSTRATE-TREATING AGENTS /11



下地処理剤No. (a)			(b)実施例用											比較例用(c)		
			S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	H1	H2	H3
下地処理剤組成 (d)	(A)	2%チタン系水性液(A1)	50	50	50	50	50							50		
		2%チタン系水性液(A2)						50								
		2%チタン系水性液(A3)							50							50
		2%チタン系水性液(A4)								50						
		2%チタン系水性液(A5)									50					
		2%チタン系水性液(A6)										50				
		2%チタン系水性液(A7)											50			
	(B)	20%ジルコニウム弗化水素酸(e)	5				2.5	10			5	10				5
		40%チタン弗化水素酸 (f)		10					20						5	
		40%珪弗化水素酸 (g)			2.5					5			5			
		10%メタリン酸 (h)				10										
	(C)	30%アクリル樹脂(C1)	10				20				20			20		
		30%アミン変性エポキシ樹脂(C2)		15				25				20			80	
		サランラテックスL-411(※1)			10				20							45
		クラレRSポリマーRS-105(※2)				25				25			40			
		脱イオン水 (i)	35	25	37.5	15	27.5	15	10	20	25	20	5	30	15	

Key: a) substrate-treating agent; b) working example use; c) comparative example use; d) composition of substrate-treating agent; e) 20% fluorozirconic acid; f) 40% fluorotitanic acid; g) 40% hydrofluosilicic acid; h) 10% metaphosphoric acid; i) deionized water; A1 through A7) 2% titanium-containing aqueous liquid; C1) 30% acrylic resin; C2) 30% amine-modified epoxy resin; *1) Saran Latex L-411; *2) "Kuraray RS Polymer RS-105.

(*1) "Saran Latex L-411": a product of Asahi Kasei Co., a vinylidene chloride resin having a solid content of 50%

(*2) "Kuraray RS Polymer RS-105": a product of Kuraray Co., a polyvinyl alcohol having a solid content of 10%

[0110] Preparation of sample coated sheets

Coating method (1)

Working Examples 1 through 11 and Comparative Examples 1 through 3

Electrogalvanized steel sheets that were 0.6 mm thick and plated at a rate of 20 g/m^2 per surface were degreased and washed. The substrate-treating preparations shown in Table 1 above were applied to the steel sheets to a dry thickness of 0.3 µm and baked under such conditions that allowed the sheets to reach a PMT (peak metal temperature) of 100°C in 15 seconds, thus preparing sample coated sheets. Next, "Cosmer 2050" (a product name, manufactured by Kansai Paint Co., an acrylic/silica composite resin solution) was applied to each treated sheet to a dry thickness of 3 µm and baked under such conditions that allowed the sheet to reach a PMT of 120°C in 20 seconds, thereby obtaining a sample coated sheet.

[0111] The obtained sample coated sheets were tested for corrosion resistance and adhesion of the upper coat. The test results are shown in Table 2 below. The tests were conducted according to the following test methods.

[0112] Corrosion resistance: The end faces and back face of the sample coated sheets were sealed. The resulting sheets were subjected to the salt spray test defined in JIS Z2371 for 240 hours. The degree of rusting of the coated surface was evaluated after the passage of 120 hours and 240 hours and rated according to the following criteria.

a: No white rust;
b: Less than 5 % of the coated surface area developed white rust;
c: From 5 % or more to less than 10 % of the coated surface area developed white rust;
d: From 10 % or more to less than 50 % of the coated surface area developed white rust;
e: 50 % or more of the coated surface area developed white rust.

[0113] Topcoat adhesion: "Amilac #1000 White" (a product name, manufactured by Kansai Paint Co., a thermosetting alkyd resin coating material, white) was applied to the sample coated sheets to a dry thickness of 30 μm and baked at 130°C for 20 minutes, thereby obtaining topcoated sheets-1. As a separate test, "Magicron #1000 White" (a product name, manufactured by Kansai Paint Co., a thermosetting acrylic resin coating material, white) was applied to the sample coated sheets to a dry thickness of 30 μm and baked at 150°C for 20 minutes, thereby obtaining topcoated sheets-2. On the coated surface of each topcoated sheets-1 and topcoated sheets-2, 11 vertical and horizontal cuts that reached the substrate were made with a knife, thereby forming 100 pieces that were each 1-mm square.

Cellophane adhesive tape was attached to this cross-cut part and rapidly peeled off. Then, the degree of peeling of the upper coat was evaluated according to the following criteria.

a: No topcoat peeling occurred at all;

b: 1 or 2 squares of the topcoat were peeled off;

c: 3 to 10 squares of the topcoat were peeled off;

d: 10 or more squares of the topcoat were peeled off.

[0114]

[Table 2]

TABLE 2 /12

	塗装方法(1)(d)				
	下地処理剤 (c) No	(e) 耐食性		(f)上層塗膜の密着性	
		120時間 (g)	240時間 (g)	(h)アミラック	(i)マジクロン
実施例 1 (a)	S1	a	b	a	a
実施例 2 (a)	S2	a	b	a	a
実施例 3 (a)	S3	a	a	a	a
実施例 4 (a)	S4	a	a	a	a
実施例 5 (a)	S5	a	b	a	a
実施例 6 (a)	S6	a	a	a	a
実施例 7 (a)	S7	a	b	a	a
実施例 8 (a)	S8	a	a	a	a
実施例 9 (a)	S9	a	b	a	a
実施例 10 (a)	S10	a	b	a	a
実施例 11 (a)	S11	a	a	a	a
比較例 1 (b)	H1	b	c	c	c
比較例 2 (b)	H2	b	d	c	c
比較例 3 (b)	H3	b	c	c	c

Key: a) working example; b) comparative example; c) substrate-treating agent; d) coating method; e) corrosion resistance; f) topcoat adhesion; g) hours; h) Amilac ; i) Magicron.

[0115] Coating Method (2)

Working Examples 12 through 22 and Comparative Examples 4 through 6

Hot dip galvanized steel sheets that were 0.4 mm thick and plated at a rate of 120 g/m^2 per surface were degreased and washed. The substrate-treating preparations shown in the foregoing were applied to the steel sheets to a dry thickness of 0.3 µm, and sample coated sheets were prepared under such conditions that allowed the sheets to reach a PMT (peak metal temperature) of 100°C in 10 seconds. Next, "KP Color 8000 Primer" (a product of Kansai Paint Co., a modified epoxy resin coating material) was applied to these treated sheets to a dry thickness of 5 µm and formed into a film under such conditions that allowed the sheets to reach a PMT of 210°C in 20 seconds. Thereafter, to this primer film, "KP Color 1580 White" (a product of Kansai Paint Co., a polyester resin coating material, white) was applied to a dry thickness of 15 µm and baked under such conditions that allowed the sheets to reach a PMT of 215°C in 40 seconds, thereby forming sample coated sheets having a topcoat film. These sample coated sheets were tested for topcoat adhesion, corrosion resistance, and moisture resistance. The test results are shown in Table 3 below. The tests were conducted according to the following test methods.

[0116] Topcoat adhesion: On the coated surface, 11 vertical and horizontal cuts that reached the substrate were made with a knife, thereby forming 100 pieces that were each 1-mm square. Cellophane adhesive tape was attached to this cross-cut part and rapidly peeled off. Then, the degree of peeling of the upper coat was evaluated according to the following criteria.

a: No topcoat peeling occurred at all;

b: 1 or 2 squares of the topcoat were peeled off;

c: 3 or 10 squares of the topcoat were peeled off;

d: 10 or more squares of the topcoat were peeled off.

[0117] Corrosion resistance: The sample coated sheets having a topcoat film were cut to a 70 mm x 150 mm size. The end faces and back face of each of the resulting sample coated sheets were sealed. Then, a 4T bent section (a section that was formed by bending the sheet at a 180-degree angle, with the coated surface facing outward and with four 0.4 mm-thick spacers sandwiched with the bent sections of the sheet) was formed on the upper part of each sample coated sheet. Further, a cross-cut portion was made on the lower part of each sample coated sheet. The resulting sheets were subjected to the salt spray test defined in JIS Z2371 for 1,000 hours. After the test, the coated sheets were evaluated for the degree of white rust development at the 4T bent section, the width of blister in the cross-cut portion, and the degree of blistering at the other general area (the center section, which was not bent or cross-cut) according to the following criteria.

[Degree of blistering in the general area]

a: No blistering;

b: Slight blistering;

c: Considerable blistering;

d: Extremely bad blistering.

[Width of blister at the cross-cut portion]

a: The blister width on one side of the cross-cut measured from the cross-cut was less than 1 mm;

b: The blister width on one side of the cross-cut measured from the cross-cut was 1 mm or larger but less than 2 mm;

C: The blister width on one side of the cross-cut measured from the cross-cut was 2 mm or larger but less than 5 mm;

d: The blister width on one side of the cross-cut measured from the cross-cut was 5 mm or larger.

[Degree of white rust development at the 4T bent section]

a: No white rust development;

b: Slight white rust development;

c: Considerable white rust development;

d: Extremely bad white rust development.

[0118] Moisture resistance: The end faces and back face of each of the sample coated sheets having a topcoat film were sealed. The resulting sheets were tested for moisture resistance according to JIS K5400 9.2.2. The test was carried out for 1,000 hours in a moisture-resistance tester box at a temperature of 49°C and a relative humidity of from 95 to 100%. The degree of blistering of the film on the coated sheets after the test was evaluated according to the following criteria.

a: No blistering;

b: Slight blistering;

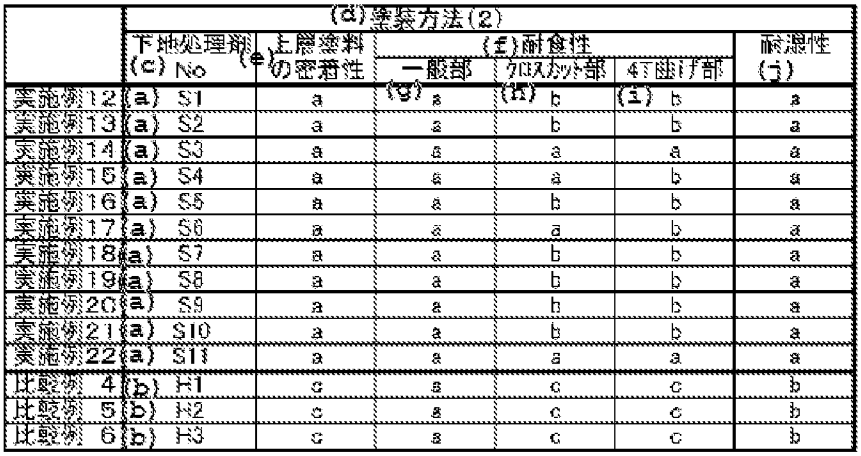
c: Considerable blistering;

d: Extremely bad blistering.

[0119]

[Table 3]

TABLE 3 /13



	(d)塗装方法(2)					
	下地処理剤 (c) No	(e) 上層塗料の密着性	(f)耐食性			耐湿性 (j)
			一般部	クロスカット部	4T曲げ部	
実施例 12	(a) S1	a	(g) a	(h) b	(i) b	a
実施例 13	(a) S2	a	a	b	b	a
実施例 14	(a) S3	a	a	a	a	a
実施例 15	(a) S4	a	a	a	b	a
実施例 16	(a) S5	a	a	b	b	a
実施例 17	(a) S6	a	a	a	b	a
実施例 18	(a) S7	a	a	b	b	a
実施例 19	(a) S8	a	a	b	b	a
実施例 20	(a) S9	a	a	b	b	a
実施例 21	(a) S10	a	a	b	b	a
実施例 22	(a) S11	a	a	a	a	a
比較例 4	(b) H1	c	a	c	c	b
比較例 5	(b) H2	c	a	c	c	b
比較例 6	(b) H3	c	a	c	c	b

Key: a) working example; b) comparative example; c) substrate-treating preparation; d) coating method; e) topcoat adhesion; f) corrosion resistance; g) general area; h) cross-cut section; i) 4T bent section; j) moisture resistance.

[0120] Coating Method (3)

Working Examples 23 through 33 and Comparative Examples 7 through 9

Electrogalvanized steel sheets that were 0.6 mm thick and plated at a rate of 20 g/m^2 per surface were degreased and washed. The substrate-treating preparations shown in Table 1 above were applied to the steel sheets to a dry thickness of 0.3 µm and baked under such conditions that allowed the sheets to reach a PMT (peak metal temperature) of 100°C in 15 seconds. Thereafter, "Magicron #1000 White" (a product of Kansai Paint Co., a thermosetting acrylic resin coating material, white) was applied to the sheets to a dry thickness of 30 µm and baked at 150°C for 20 minutes, thereby obtaining sample coated sheets.

[0121] The obtained sample coated sheets were tested for corrosion resistance and coated-film adhesion. The test results are shown in Table 4 below. The tests were conducted according to the following test methods.

[0122] Adhesion of coated film: On the coated surface, 11 vertical and horizontal cuts that reached the substrate were made with a knife, thereby forming 100 pieces that were each 1-mm square. Cellophane adhesive tape was attached to this cross-cut part and rapidly peeled off. Then, the degree of peeling of the topcoat was evaluated according to the following criteria.

a: No topcoat peeling occurred at all;
b: 1 or 2 squares of the topcoat were peeled off;
c: 3 to 10 squares of the topcoat were peeled off;
d: 10 or more squares of the topcoat were peeled off.

[0123] Corrosion resistance: The end faces and back face of each of the sample coated sheets were sealed. The resulting sheets were subjected to the salt spray test defined in JIS Z2371 for 240 hours, after which the degree of rust development at the general coated area and the degree of blistering of the cross-cut portion were evaluated according to the following criteria. In addition, the cross-cut portion was peeled off with a tape, after which the width (mm) of the section from which the coated film was peeled off was measured for each sample sheet.

[Degree of white rust development at the general area] a: No white rust development;

b: Less than 5% of the coated surface area developed white rust;

c: From 5% or more to less than 10% of the coated surface area developed white rust;

d: From 10% or more to less than 50% of the coated surface area developed white rust;

e: 50% or more of the coated surface area developed white rust.

[Width of blister at the cross-cut portion]

a: The blister width on one side of the cross-cut measured from the cross-cut was less than 1 mm;

b: The blister width on one side of the cross-cut measured from the cross-cut was 1 mm or larger but less than 2 mm;

C: The blister width on one side of the cross-cut measured from the cross-cut was 2 mm or larger but less than 5 mm;

d: The blister width on one side of the cross-cut measured from the cross-cut was 5 mm or larger.

[0124]

[Table 4]

TABLE 4

	(d) 塗装方法(3)				
	下地処理剤 (c) No	塗膜の (e)密着性	(f) 耐食性		
			一般部	クロスカット部	クロスカット部／テープ、剥離巾
実施例23	(a) S1	a	(g) a	(h) b	(i) 2.0mm
実施例24	(a) S2	a	a	b	2.0
実施例25	(a) S3	a	a	a	1.0
実施例26	(a) S4	a	a	a	1.5
実施例27	(a) S5	a	a	b	2.5
実施例28	(a) S6	a	a	a	1.0
実施例29	(a) S7	a	a	b	2.0
実施例30	(a) S8	a	a	b	2.0
実施例31	(a) S9	a	a	b	3.0
実施例32	(a) S10	a	a	b	2.5
実施例33	(a) S11	a	a	a	1.0
比較例7	(b) H1	c	a	c	10.0
比較例8	(b) H2	c	a	c	7.0
比較例9	(b) H3	c	a	c	5.0

Key: a) working example; b) comparative example; c) substrate-treating preparation; d) coating method; e) film adhesion; f) corrosion resistance; g) general area; h) cross-cut section; i) cross-cut section/tape peeling width.

[0125] Coating Method (4)

Working Examples 34 through 44 and Comparative Examples 10 through 12

Aluminum sheets (#5182) that were 0.27 mm thick were degreased and washed. The substrate-treating preparations shown in Table 1 above were applied to these sheets to a dry thickness of 0.3 µm and baked under such conditions that allowed the sheets to reach a PMT (peak metal temperature) of 100°C within 15 seconds. Thereafter, a clear coating material composed of 80 parts of "Epikote 1009" (a product of Japan Epoxy Resin Co., a bisphenol A epoxy resin, epoxy equivalent weight: 3,500, number-average molecular weight: 3,750), 20 parts of "Hitanol 4020" (a product of Hitachi Kasei Kogyo Co., a phenol resin), and 0.4 part of phosphoric acid was applied to the sheets by a roll coater so as to have a dry film weight of 120 mg/cm^2 and run through a hot-air conveyor oven, thereby obtaining baked sample coated sheets. With respect to the baking conditions, the PMT was set to 240°C, and the time spent to go through the oven was set to 20 seconds. The obtained sample coated sheets were subjected to various tests according to the following test methods. The test results are shown in Table 5 below.

[0126] Test Methods

Processability: A special Pittsburgh-lock-type Dupont impact tester was used for this test. A sample coated sheet was folded in two at the lower portion, with the coated surface facing outward, and a 0.3 mm-thick aluminum sheet was inserted at the bent section. The thus-prepared test sheet was placed inside the tester, and a 1 kg-thick [sic] iron weight having a flat contacting surface was dropped onto the test sheet from 50 cm above, thereby applying an impact to the bent portion. Thereafter, a voltage of 6.5 V was applied to the tip of the bent portion for 6 seconds, and the current value (mA) of the 2 mm-wide tip part of the bent portion was measured and evaluated according to the following criteria.

⊙: The current value was smaller than 0.5 mA;

○: The current value was 0.5 mA or larger but smaller than 1.0 mA;

△: The current value was 1.0 mA or larger but smaller than 5.0 mA;

X: The current value was 5.0 mA or larger.

[0127] Corrosion resistance of processed section: Using a can-top pressing machine, the sample coated sheets were made into can tops.

These can tops were seamed onto the can bodies that were filled with an aqueous solution prepared by dissolving 2 parts of malic acid, 2 parts of citric acid, and 2 parts of table salt in 100 parts of deionized water. With the coated surface of the sample sheets that were formed into can tops immersed in the content of the cans, the cans were stored inside a 50°C room for 5 days. Then, the cans were cut open, and the condition of the can tops was observed and evaluated according to the following criteria.

⊙: No abnormality observed with the can top;

○: No rust was observed on the can top, but very slight change was seen;

△: Some rust was observed on the cap top;

X: The can top showed a considerable degree of rusting.

[0128] Resistance to film remaining (Anti-feathering property):

The sample coated sheets were formed into can tops in the same manner as in the case of evaluating processed-section corrosion resistance. After these can tops were soaked in 100°C boiling water for 10 minutes, the opening section of each can top, with the coated surface facing downward, was pulled upward and opened. The width of the coated film that was peeled off from the edge of the opening was measured and evaluated according to the following criteria.

⊙: The maximum peeled width of the coated film was less than 0.2 mm.

○: The maximum peeled width of the coated film was 0.2 mm or more but less than 0.5 mm.

△: The maximum peeled width of the coated film was 0.5 mm or more but less than 1.0 mm.

X: The maximum peeled width of the coated film was 1.0 mm or more.

[0129] Retort whitening resistance: A sample coated sheet was immersed in water and treated in an autoclave at 125°C for 30 minutes, after which the whitening of the coated film was evaluated according to the following criteria.

⊙: No whitening at all;

○: Very slight whitening;

△: Slight whitening;

X: A considerable degree of whitening.

[0130] Sanitation: A sample coated sheet and tap water that had been treated with active carbon were placed in a heat-resistant glass bottle, with a ratio of 1 cc of the active-carbon-treated tap water per 1 cm^2 of the coated area of the sample coated sheet, and a cap was placed on the bottle. The bottle was treated in an autoclave at 125°C for 30 minutes, and the liquid content of the bottle after the treatment was evaluated for sanitation based on the consumed quantity (ppm) of potassium permanganate in accordance with the test method described in the Food Sanitation Law.

⊙: 1 ppm or less consumption;

○: 1 ppm or more but less than 3 ppm consumption;

△: 3 ppm or more but less than 10 ppm consumption;

X: 10 ppm or more consumption.

[0131] Adhesion: A nylon film was sandwiched between two pieces of each sample coated sheet (150 x 5 mm), with the coated surfaces thereof as the surfaces to be bonded, and they were heated at 200°C for 60 seconds and subsequently pressed at 200°C for 30 seconds, thereby fusing and bonding the nylon film to both coated films, and this was used as a test piece. Next, the T-type peeling strength of this test piece was measured with a tensile tester (Shimazu Autograph AGS-500A) at a pull rate of 200 mm/minute and a temperature of 20°C. The average of 5 measurement results was graded according to the following criteria. /15

⊙: 3 kg/5 mm or higher;

○: 2 kg/5 mm or higher but lower than 3 kg/5mm;

△: 1 kg/5 mm or higher but lower than 2 kg/5mm;

X: Lower than 1 kg/5 mm.

[0132]

[Table 5]

TABLE 5

	(d) 塗装方法(4)						
	下地処理剤 (c) No	加工性 (e)	加工部 (f)耐食性	耐膜残 (g)り性	耐レトルト (h)白化性	衛生性 (i)	接着性 (j)
実施例34	a) S1	◎	◎	○	○	◎	○
実施例35	a) S2	○	○	◎	○	○	◎
実施例36	a) S3	◎	○	○	◎	◎	○
実施例37	a) S4	○	◎	○	○	○	◎
実施例38	a) S5	◎	○	◎	◎	○	○
実施例39	a) S6	◎	○	◎	○	◎	○
実施例40	a) S7	○	◎	○	○	○	◎
実施例41	a) S8	◎	○	○	◎	○	○
実施例42	a) S9	○	◎	○	○	○	◎
実施例43	a) S10	◎	○	○	◎	○	○
実施例44	a) S11	○	◎	◎	○	◎	○
比較例10	b) H1	○	○	△	○	○	×
比較例11	b) H2	△	△	△	○	○	△
比較例12	b) H3	○	△	○	◎	○	△

Key: a) working example; b) comparative example; c) substrate-treating preparation; d) coating method; e) processability; f) processed-section corrosion resistance; g) resistance to film remaining; h) retort whitening resistance; i) sanitation; j) adhesion.